CALCULATED OH-STRETCHING VIBRATIONAL SPECTRA OF HYDRATED COMPLEXES

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We have calculated fundamental and overtone OH-stretching vibrational band positions and intensities for small water clusters and hydrated complexes. Results for the water dimer and hydrated complexes of oxygen, nitrogen, formic acid and nitric acid are discussed. The spectral intensities were determined with the harmonically coupled anharmonic oscillator (HCAO) local mode model and *ab initio* calculated dipole moment functions. The dipole moment functions were calculated with the HF, QCISD and B3LYP levels of theory. Overtone spectra of these clusters have not been observed, and local mode parameters were obtained from scaled *ab initio* calculations. Our calculations predict that the frequencies of the hydrogen-bonded OH-stretching transitions are red-shifted compared to those of the monomers and that the shifts increase with increasing hydrogen bond strength. For the fundamental region, we see a significant increase in intensity for the hydrogen-bonded transitions compared to the monomer transitions. For the first overtone, the hydrogen-bonded transitions are weaker than the monomer transitions, and for the higher overtones the intensities are comparable. We find that the B3LYP method overestimates the bonding interaction, whereas the HF method slightly underestimates the interaction compared to results obtained with the QCISD method. Our HCAO approach provides simulated spectra, which can guide experimental efforts to observe transitions in these complexes and we have used the spectra of water dimer to assess its impact on absorption of solar radiation.